TDEP Committee Meeting April 23, 2012, Portland Oregon

1. Welcome and introductions

- Self introductions by all attendees (see attached attendance list)
- Explanation by Gary Lear for reason for TDEP committee
 - Focal point for discussion of new ideas
 - To derive accurate total deposition estimates for a variety of parameters

2. Presentation of TDEP Needs Table (Donna Schwede)

- Purpose of Needs Table to communicate ongoing, planned and needed work.
- With lack of, or shrinking, funding the table can help prioritize needs and provide agencies/groups with a document to point to for research proposals
- Living table. People are to help TDEP committee to add, correct, edit table. Donna is contact person for updates
- Donna reviewed the study areas listed in the table by category, i.e. Direct Dry Deposition Measurements, Routine Monitoring, Model Improvements and Evaluation, etc.
- Table in spreadsheet format so it could be sorted based on one's interest
- The Model Improvements and Evaluation category is missing the Canadian model
- Study areas identified as 'needed' in the Measurement Improvements/Methods Development category need to be developed in order to be implemented

Discussion:

- Alan VanArsdale: we are missing particles such as pollen and dust. Also noted that stem flow and throughfall are not in the table
- Rick Artz: where are the edges of this table? Do we stay with just S, N and Hg or do we expand to add in pollen, dust, etc. If we want to expand then we will need met data sets. Climate reference data sets are now available
- Rick Graw: emission inventories need to be updated. Donna said there is schedule for updating 2008 will be out soon and 2011 after that.
- Great interest in emissions backcasting. Rich Sheffe : backcasting of emissions is not routinely done. Important for looking at trends. Some EPA and DOE grant funding going into backcasting aerosol climate emissions. Also STAR grant opportunities
- Gary Lear: Difficulty in making progress with EPA for need of backcasting rather than always developing new emission models. Rich S agreed that EPA has always been focused on forecasting forward.
- Need emissions modeling framework. Start with 2008 and use this year to develop.
- Donna: need to look at historical emissions inventories for critical loads modeling. Past emissions inventories are not consistent due to use of changing models used to develop them. A uniform way of backcasting is necessary to create uniform data set
- The drive for backcasting has to come from ecosystem scientists as EPA is always going to be looking forward
- Dave Schmeltz: resources are needed and can we use the table to prioritize the needs and raise awareness? Donna said that this is part of table's purpose. Should table be converted into a formal report to use with EPA management and others such as STAR grant funders?

- Kristi Morris: currently the table is a laundry list and we should have the group prioritize about 5 research areas and then produce report summarizing the needs
- Gary: CASTNET has a small budget for addressing total deposition and ideas and priorities from TDEP would help guide this work
- Brett Schichtel: How do we prioritize table since it is multidimensional? Priorities will change based on interest area. Should table be more defined? Does Hg belong in here?
- Pam Padgett: Hopeful that modeling and measurement communities would meld together as a result of this document as currently there is a schism between the two communities
- Brett: How to build model is missing
- Rick A: Does this group want NO2 estimates via remote sensing? Donna said we can also get leaf out and LAI values from remote sensing
- Mae Gustin: Modelers can guide where measurements should be made, but we need to decide what to measure first. The TDEP committee should focus on what we are getting from current measurements
- Donna: Dry deposition point measurements cannot be spatially interpolated. Hence the need for models. Models and point measurement data need to be worked together.
- Mae: There are areas where measurements and models do not work together well. Models are assumed to be correct
- Rich S: Not so, but a lot of people out there don't know this and take model results as gospel
- Rick Graw: AMNet data needed for regulations and assessment of regulations (ie. MATS). We need more source monitoring. Add a column for applications to help prioritize the table.
- Rick A: We need to understand priorities and applications. As far as Hg, where are we going with it?
- Rich S: Would like to see more info in table. Under N would like to add species such as HNO3, NO2, etc.
- **3.** Replacement of Dry Deposition Velocities (Vd) at CASTNET Sites (cont'd) (Gary Lear) This presentation is on the TDEP webpage:

<u>http://nadp.sws.uiuc.edu/committees/tdep/</u> Please refer to presentation for further information than provided in these minutes

- If any met parameters missing, the hourly deposition velocity (Vd) also missing
- Without CASTNET met measurements, no choice but to use models
- Different methods of estimating Vd investigated
- Short term Vd (hours or days) really impacted by local meteorology, but longer time scales are dominated by site-specific seasonal trends
- Seasonal variation consistent from year to year; variance of each week similar from year to year
- CASTNET database will have a mixture of real and imputed values and they both have some, but different degrees of autocorrelation
- Task was to quantify uncertainty of replacement scheme

- Compared complete, non-missing data set with one that was imputed to compare differences
- Uncertainty values calculated for different scenarios such as 50 versus 100% missing data
- How does uncertainty compare with percent replaced and how to apply to network?
- Mean and standard deviation for site based on historic CASTNET database for the season and parameter are needed for estimation of uncertainty for specific site, season and parameter as well as percentage of missing data for site-year
- Comparison of imputed with actual shows no bias but there is some spread
- Uncertainty values are site-specific
- There is a web site that demos how imputed values affect the data: <u>http://epa.gov/castnet/javaweb/mcannual replaced.html</u>

Discussion/questions:

- Eric Prestbo: Are missing data random or not? Some are and some have some seasonal pattern
- Pierrette: Why not replace met first rather than Gary's method? Gary looked at this but it was harder to estimate uncertainty of the replaced met. Donna noted that using modeled met was investigated and weather forecasting met did not work so well at complex terrain sites. Sensitivity analyses were performed to determine what parameters were most important to model
- Gary concluded that he has further work to do as far as developing more models

4. Measuring Total Reactive Nitrogen and its Composition (Brett Schichtel) This

presentation is on the TDEP webpage (<u>http://nadp.sws.uiuc.edu/committees/tdep/</u>). Please refer to presentation for further information than provided in these minutes

- Task is to determine the important components of reactive N (RN), how to measure, how to model, and tools for assessing causes of excess reactive N deposition (such as source apportionment)
- The following studies have contributed information:
 - 1. ROMANS II: Characterization of total RN deposition and its sources at Rocky Mountain NP (from November 2008 through November 2009)
 - 2. GrandTReNDS: Grand Teton RN deposition study (from April through September 2011)
 - 3. IMPROVE NH₄, NH₃ and amines measurement study (from April 2011 through August 2012)
 - 4. CSU: Colorado front range passive NH₃ network
 - 5. Modeling of RN in Rockies using CAMx (Barna et.al.)
 - 6. Snow pack Chemistry George Ingersoll to send 2011-2012 snow pack samples to CSU for analysis of organic N (ON), NO₃, NH₄ and SO₄
 - 7. New fine particulate total N measurement (Chow and Watson)
- Detailed information presented on the GrandTReNDS study
- Purpose of study was to determine total N deposition in Grand Teton and its composition as well as to determine the origin of deposited N
- Further information on DRI analysis via thermal optical reflectance (TOR)

Discussion:

- Tom Butler: Was the ON in particulate form or water soluble? Brett answered that 20% was wet ON and only a small portion was particle ON. So, mainly wet organic
- Rick Artz: Commented that some of this 'stuff' is so unstable. Brett said that although collection occurred within a few hours at some locations there is no way to deal with this issue. Rick added that some will be bioavailable and some will be very local that it may not matter. However, needs to be dealt with
- Rick Graw: Can we come up with permitting rules based on this data? How to use this data in modeling? Can we back calculate how much NH₃ to neutralize?
- Donna: wants to improve estimates of NH₃ in CMAQ. Bidirectional models do very well in the east.
- Pam Padgett: There is some chemistry in the southwestern US that is not represented (especially the 4-corners area) in models which focus more on eastern US
- Mae: Does not think we have enough long term data in the Grand Tetons and she is not confident of snow pack measurements for NH₃, but how are they for N?
- **5. CASTNET: Ameriflux Deposition Study (Greg Beachley)** This presentation is on the TDEP webpage (<u>http://nadp.sws.uiuc.edu/committees/tdep/</u>). Please refer to presentation for further information than provided in these minutes
 - Objective of study to find out if CASTNET filter packs (FP) can be used at different heights to provide reliable method for integrated deposition of pollutants
 - Also, can filter pack data be used along with met measurements to evaluate performance of MLM?
 - Ameriflux established in 1996 with 102 sites for continuous observation of ecosystem level changes of CO₂, water, energy and momentum fluxes
 - Two CASTNET FPs installed above and below canopy at the AmeriFlux site in Howland, ME.
 - Eight O₃ inlets throughout canopy sampled with one analyzer via sequential sampling
 - Inlets situated to capture LAI inflections. LAI greatest at 14 m
 - NO₃ shows more difference above and below canopy then NH₄. Above canopy NO₃ is higher
 - SO₄ does not show as much difference but more so than NH₄
 - Above canopy SO₂ is substantially higher
 - O₃ data show that higher concentrations correlate better. Much more of a spread of concentrations at 50 ppb or lower
 - Above canopy O₃ values correlate well with no significant differences
 - Below canopy (2 m) show episodic differences that usually happen at night but not every night. This is not necessarily seasonally dependent

Discussion:

- Mae: commented that there is line loss of O_3 from the top because it is highly reactive. Suggested putting analyzer at the top to avoid this.
- Pam: Suggested using equal line lengths regardless of height because it does make a difference.

- Alan V: Asked how the O₃ standard was sent and would AMEC mind if he stopped by the site. Alan's group does probe analysis for all sites and they would be happy to provide audit. Alan's group also considering doing this with NEON.
- Pam: Suggested putting FP at peak LAI to see what is happening with HNO₃ deposition
- 6. Recent Results and Future Plans for Nitrogen Flux Measurements at Duke Forest, NC (John Walker)
 - Ammonia exchange in hardwood canopy at Duke Forest Ameriflux site
 - Also sampling HONO, HNO₃, HCl, SO₂ and turbulence
 - Purpose to estimate above and below canopy fluxes.
 - Above canopy fluxes estimated via aerodynamic gradient method and in-canopy fluxes via inverse Lagrangian dispersion modeling
 - HNO₃ shows very steep drop from above to below canopy; HCl has relatively steep drop as well; SO₂ drops below canopy crown;
 - Daytime profiles indicate NH3 emission from the forest floor and deposition from atmosphere to canopy
 - Review of ongoing work

7. Amino Acids (AA) as a Component of ON in PM2.5 (John Walker)

- This work motivated by need to better understand composition and sources of ON in atmospheric aerosol and contribution of organics to dry deposition of N
- Sources of atmospheric AA's are biomass burning, marine emissions, suspension of plant material, soil biological material, pollen, fungi, bacteria, spores
- Contribution of AA to bulk ON fraction not well characterized
- Samples collected on Teflon filters for 12-24 hours and analyzed immediately by LC-MS (Q-TOF)
- FAA and CAA in PM2.5 measured at site in summer 2010 represent 2.5% and 4.7% of total ON measured
- Review of ongoing work

8. Development of an Integrated Flux Measurement System for Quantifying N and S Dry Deposition Budgets (John Walker)

- MARGA work
- Direct flux measurements of primary N and S compounds are needed for a variety reasons
- In collaboration with others, EPA/ORD assembling an integrated flux measurement system
- Review of ongoing and future work

Discussion:

- Brett: interested in NH₃ emissions from forest floor. Asked if any soil samples were taken to determine soil emissions rather than just from soil floor (litterfall)? Exchange right at soil surface is very complicated but Walker's group will explore this further.
- Brett also interested in the NOy box and methodology

9. Brief Update on Urban Deposition Monitoring Network (Tom Butler)

- This network will start with measuring wet deposition
- Still in planning stages and looking to get their money together
- Interested in having a session at the Fall meeting
- Network could be folded into NTN, but sites would have to be truly urban
- Have not gotten as far as considering dry deposition
- They are considering passives for some measurements
- Kathy commented that it might be helpful to steer their topics for Fall meeting

10. Progress on Investigating the Use of Surrogate Surfaces and Passive Samples for Measuring Atmospheric Mercury (Mae Gustin)

- Tekran's used for measuring atmospheric Hg
- Surrogate Surfaces (SS): open surface facing down; collect GOM but fine aerosols cannot be ruled out.
- Collection depends on turbulence but same as any ecosystem
- Passive samplers measure concentrations. Sampling rate based on Fick's Law
- Tekran's, SS and PS samplers are not showing same trends
- Modeled dry deposition is also not tracking in that modeled values are much lower
- Passive sampler measurements do not usually agree with Tekran GOM measurements
- Investigating gold and silver surfaces although gold not very good as a passive surface
- Silver still needs exploring and analytical methods need further testing
- The Tekran has a finer temporal resolution and we need to understand what the Tekran is actually measuring
- Both passives and Tekrans are telling us something but not clear what yet
- Overall information derived from PS and SS samplers can be used to refine the Tekran system
- Can also help us better understand the chemistry and behavior of Hg in the atmosphere

Discussion:

- Eric Prestbo: Hg research has been hampered by lack of funding and they therefore do not understand reaction rates and different forms of Hg
- Pierrette: we need to understand the uptake and the species
- Krish Vijayaraghavan: How to translate deposition to a homogeneous surrogate surface to real life
- Mae: GOM deposited to a leaf can be readily released back to the atmosphere. Leaves are like a passive sampler surface
- Eric P: A number of really good observations have come out but they are observationally defined. The SS are seeing something different yet. Hampered by the fact a standard cannot be generated in the field

11. Estimating Dry Deposition of Reactive Gaseous Mercury Using Selective Adsorption Membranes at MDN Sites (Bob Brunette) This presentation is on the TDEP webpage (<u>http://nadp.sws.uiuc.edu/committees/tdep/</u>). Please refer to presentation for further information than provided in these minutes

- Passive RGN Pilot Study (2009-2011)
- Low cost, easy to deploy and operate
- Can be deployed on a network scale
- Seven sites, 5 collocated with MDN, one site collocated with Tekran
- Review of why both MDN passive RGM and AMNET RGM networks
- Role of Hg Networks
- Bob agrees with Eric P that all hampered by the inability to come up with a standard
- **12. Mercury Dry Deposition Collaboration (David Gay)** This presentation is on the TDEP webpage (<u>http://nadp.sws.uiuc.edu/committees/tdep/</u>). Please refer to presentation for further information than provided in these minutes
 - Collaboration between Environment Canada and NADP
 - Goal is to estimate the dry deposition at all AMNet sites of
 - GEM, partial
 - GOM
 - Particulate Bound Mercury < 2.5 microns (PBM2.5)
 - Environment Canada will produce weekly dry deposition velocities of the individual fractions
 - NADP will use the Vd's along with average atmospheric concentrations to estimate dry deposition of the Hg fractions
 - Vd will be calculated by use of grid-based meteorology produced from the Canadian weather forecast model, AMNet site characteristics and atmospheric concentrations and the big-leaf dry deposition model
 - Products would be:
 - Weekly dry deposition estimates of GOM and PBM2.5
 - Downward dry deposition of GEM
 - Weekly wet deposition from MDN
 - Weekly dry deposition from AMNet
 - Possible litterfall work in the future
 - Donna: ORD is also working on the bi-directional flux for Hg. The results will be available for NADP to use.

13. Wet Organic Nitrogen: Recent Studies (Chris Lehmann)

- Study funded by John Walker's group (EPA)
- 54 NTN sites
- At 6 sites looked at filtered versus unfiltered samples
- Conducted intensive field study at BVL130 where daily AIRMoN samples were compared with weekly NTN samples as well as samples collected with refrigerated collector
- Refrigerated collector would be most conducive for network deployment
- There is a negative bias of AIRMoN and NTN ON results against refrigerated; NTN bias is largest
- Significant losses of ON when not refrigerated
- Effect of ambient temp was also considered

- Lower ambient temp, better correlation
- Higher ambient temp, worse correlation
- Sample storage length was looked at from all sites
 - The greatest scatter was when samples stored at room temp
 - But this stabilized when samples refrigerated
- Effect of filtration: filters are adding a small amount of ON
- Seasonal differences can be seen in N
- More N deposition in summer
- Lots of uncertainty in data
 - Positive bias from filtration
 - Event sampling versus weekly
 - Ambient temperature
 - Transit time
- Produce a map of N deposition with uncertainty level applied
- AIRMoN protocol best for N
- Few differences between daily sample and reference collector
- If event sampling can't be done, then deploy refrigerated collector
- If this is not possible, then expedited shipping
- ON measured by difference: Subtract sum of NH4 and NO3 from total N

Discussion:

- Rick Artz: were old critiques taken into consideration? Chris says they have been for the NADP NH₄ method. Rick also suggested setting up a collector at ISWS and analyzing sample immediately upon rain ending and then analyzing it again the next AM to quantify how much loss.
- Study summer samples most since these would be most affected by ambient temps
- Tom Butler: Where is the filtration bias coming from? Tracy Dombek said bias was organic.
- Tom: where are these results going? Are we implementing?
- Chris Lehmann: problem is the digest method. Not too feasible.
- Butler: why not do it as special study rather than network wide?
- Alan V: Have older filters been compared to newer filters?
- Chris L: Only one batch of filters used for study. All same age
- Brett: Do N losses increase with ambient temp? As an ecologist he is interested in bioavailability. What happens to ecosystem when it gets deposited? What is the residence time in ecosystem versus volatility rate of system?

14. GENERALGROUP DISCUSSION:

A. TDEP Sponsored N Flux Measurement Workshop

- John Walker: Committee considering TDEP organized N flux measurement techniques workshop for Fall 2013. Is anybody interested in something like this? This would be an opportunity to bring people in from Ameriflux, CA groups, SOAS, modeling groups from Canada and scientists from outside of the US.
- Gary: Should this be part of NADP meeting or an independent meeting? Initial thoughts were that it would be tough to make part of Fall meeting, but Gary thinks

there might be lots of spare time and if schedule condensed to make the meeting 4 days then we could get it all in.

- Precedent for this workshop is the NH₃ workshop that was held in DC about 10 years ago
- TomB: Can workshop be held all in one day? John W thinks we can cover a lot in one day but at least 1 ½ days would be better to attract people from overseas.
- If not part of NADP and separate meeting, then travel funds may become an issue
- Group interested. Nobody against the idea. So TDEP will go ahead with plans

B. GOALS of TDEP

- Gary: What are we trying to accomplish in TDEP? Do we want topics to have more focus?
- Alan V: Figure out the questions, then figure out what measurements and research needs to be done. Come up with core questions and then bins of info to answer those core questions
- Gary: This is similar to the Objectives column that was suggested for the Needs Table and TDEP has objectives but there is a huge diversity of institutional interest represented
- Rick A: Wish list will have some things I common even if put together by disparate groups (1st tier). Then 2nd tier would be where we are making progress. The 3rd tier would involve the tougher questions as far as methodology. The last level would be the specific tools needed by some part of community (ecosystem, atmospheric chemists, etc.). The basic measurement systems should be thought of first. Key basic measurements of S and N and maybe Hg and NH₃ need to be put up, signed, sealed and delivered
- Eladio: Is there a product that comes out of this committee or this just meeting and discussion?
- Gary: so far it has been just meeting and discussion
- Greg Weatherbee: Where is the group going and what is the conceptual model for making products? Needs a little more organization and structure. Don't just talk about what others have done. Need concrete results
- Rich Scheffe: What's wrong with extending it more? Put product out there for current deposition of S and N estimates. Maybe Hg?
- Gary L: For next meeting ID what products should be and how to get them out there
- Rich: This cannot be an emphasis on measurement. It's too complicated since we can't actually measure. But the beauty of the group is that it consists of modelers as well as measurement people
- Pierrette: ID and prioritize gaps in knowledge. Group's mandate could be to take laundry list and prioritize. Could focus on different gaps each year with a white paper at the end. Come up with a set of recommendations.
- Gary: Leary of products but can deal with recommendations
- Donna: In order to deal with uncertainties and gaps it might help to define and quantify the uncertainties. Then we can say why it is a priority.

- Gary: The difference between the TDEP committee and other NADP groups is that this group is less formal and we can have more discussion
- Rich S: National meeting is broader in scope. Can focus better in this format.
- Brett: The total N budget has never been discussed this specifically
- Rich S: Philosophically, deposition has been looked at as a secondary issue. Very little attention given to it. We should also question how we characterize other systems because they are not taking deposition into account. This is a serious problem as policy makers do not understand that deposition is the impact and not air quality
- Rick Graw: Can we bracket some of the deposition problems? Like how much overestimation of N?
- Brett: Instead of generating product, what product could we get? Map of the world of total deposition of certain species?
- Rick G: Is the focus ecosystem? Need to bring in end users such as ecosystem folks

C. WRAP-UP (Kristi Morris)

- TDEP has 1 ½ hours on CLAD agenda and this is where we can mesh with some end users and can get more focused on creating products. CLAD probably wants maps of best available data products that they can use with a quantified uncertainty
- Fall meeting in Portland Maine. Full day TDEP meeting scheduled. Should it be Monday or Friday? Friday worked well in Providence
- We will be breaking up into small discussion groups in the Fall and then come back together as the larger group and summarize results from small group
- Donna: Please send additions and corrections to her but ID where it should go in Table

Meeting adjourned